(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 214 448 A2

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 86110587.2

(22) Date of filing: 31.07.86

(51) Int.Cl.[4]: C 09 D 5/03
C 09 D 3/48, C 08 G 59/40

(30) Priority: 07.08.85 US 763377

(43) Date of publication of application: 18.03.87 Bulletin 87/12

(84) Designated Contracting States: BE DE FR GB IT NL SE

(71) Applicant: PPG INDUSTRIES, INC.
One PPG Place
Pittsburgh Pennsylvania 15272(US)

(72) Inventor: Pettit, Paul Herschel, Jr.
1800 Foxcroft Lane
Allison Park PA 15101(US)

(74) Representative: Sternagel, Hans-Günther, Dr. et al.
Patentanwälte Dr. Michael Hann Dr. H.-G. Sternagel
Sander Aue 30
D-5060 Bergisch Gladbach 2(DE)

(54) Powder coating compositions of polyepoxides and acrylic copolymers.

(57) A thermosetting powder coating composition and a coated article are disclosed. The composition comprises a coreactable particulate mixture of an acid group-containing acrylic polymer and a compatible epoxy novolac resin and an incompatible epoxy resin. The compositions have a good balance of properties and are useful as coatings for appliance, general industrial and automotive applications.

REFERENCE AU

0214448

POWDER COATING COMPOSITIONS OF POLYEPOXIDES AND ACRYLIC COPOLYMERS

Background of the Invention

Field of the Invention: The present invention relates to thermosetting powder coating compositions, and more particularly to powder coating compositions based on acrylic copolymers and polyepoxides.

Brief Description of the Prior Art: Powder coating compositions for use in painting of surfaces are extremely desirable. Such coating compositions greatly reduce and can even eliminate the organic solvents used in liquid paint compositions. When the powder coating composition is cured by heating, little if any volatile material is given off to the surrounding environment. This is a significant advantage over liquid paint compositions in which organic solvent is volatilized into the surrounding atmosphere when the coating composition is cured by heating.

The present invention provides powder coating compositions which have a superior balance of properties relative to the commercially available powder coating compositions. The powder coating compositions of the present invention provide a resultantly cured coating which is hard and glossy, has good adhesion, flexibility and impact resistance, along with good resistance to salt spray, caustic and organic solvents.

Summary of the Invention

In accordance with the present invention, a thermosetting powder coating composition comprising a coreactable particulate mixture of ingredients is disclosed. The mixture comprises:

(A) an acid group-containing acrylic copolymer having a

100°C. and a number average molecular weight of 1500 to 20,000,

(B) an epoxy novolac resin which is compatible with (A), and

(C) an epoxy resin which has a number average molecular weight of at least 1000 and which is incompatible with (A).

Detailed Description

The powder coating compositions of the present invention comprise an intimate mixture of several materials. One material of the mixture is an acid group-containing acrylic polymer having a number average molecular weight of 1500 to 20,000, preferably 2000 to 20,000 and a glass transition temperature (Tg) in the range of 40 to 100°C., preferably 50 to 80°C. The acrylic polymer provides for hardness, gloss and solvent resistance in the resultant coating.

The molecular weights of the acrylic polymers are determined by gel permeation chromatography (GPC) using a polystyrene standard. Therefore, it is not the actual molecular weight which is measured but an indication of the molecular weight as compared to polystyrene. The values which are obtained are commonly referred to as polystyrene numbers; however, for the purpose of this application, they are referred to as molecular weights.

If the number average molecular weight is below 1500, the solvent resistance and mechanical strength of the coating is poor. Molecular weights higher than 20,000 are undesirable because the melt flow of the polymer is poor resulting in a rough coating.

The Tg of the polymer is a measure of hardness and melt flow of the polymer. The higher the Tg, the less the melt flow and the harder the coating. Tg is described in Principles of Polymer Chemistry (1953), Cornell University Press. The Tg can be actually measured or it can be calculated as described by Fox in Bull. Amer. Physics Soc. 1, 3, page 123 (1956). Tg as used herein refers to the calculated values unless the value cannot be calculated, and in this instance the Tg refers to the actually measured values. For measurement of the Tg of the polymer, Differential Scanning Calorimetry can be used (rate of heating 10°C. per minute, Tg taken at the first

If the glass transition temperature is below 40°C., the powder tends to be sticky and difficult to handle. If the glass transition temperature is greater than 100°C., the melt flow of the polymer is too low and the coating will have poor appearance.

The acid group-containing acrylic polymer is preferably a carboxylic acid group-containing acrylic polymer and can be formed by reacting a polymerizable alpha, beta-ethylenically unsaturated carboxylic acid with one or more other polymerizable alpha, beta-ethylenically unsaturated monomers, particularly vinyl aromatic monomers and esters of alpha, beta-ethylenically unsaturated carboxylic acids.

Examples of the carboxylic acid group-containing monomers which can be used are acrylic acid and methacrylic acid, which are preferred, as well as crotonic acid, itaconic acid, fumaric acid, maleic acid, citraconic acid, and the like, as well as monoalkyl esters of unsaturated dicarboxylic acids such as itaconic acid, fumaric acid, maleic acid, citraconic acid, and the like. The acid group-containing monomer is preferably present in the polymer in amounts of about 3 to 25 percent, more preferably from about 5 to 20 percent by weight based on total weight of the monomers. Amounts less than 3 percent result in poorer solvent resistance and poorer mechanical strength of the coating.

Examples of vinyl aromatic compounds are monofunctional vinyl aromatic compounds such as styrene which is preferred, toluene and alkyl-substituted styrenes such as toluene and chloro-substituted styrene such as chlorostyrene. The vinyl aromatic monomer is preferably present in the composition in amounts of about 25 to 75, more preferably from about 40 to 75 percent by weight based on total weight of the monomers. Amounts less than 25 percent result in poor detergent resistance, whereas amounts greater than 75 percent result in poor flexibility.

Examples of the esters of the alpha, beta-ethylenically unsaturated acids are esters of acrylic and methacrylic acid and include methyl methacrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, dodecenyl acrylate, methyl methacrylate, ethyl methacrylate, N-butyl methacrylate, and 2-ethylhexyl methacrylate. Preferably, these esters are present in amounts of about 5 to 70, more

preferably from about 10 to 50 percent by weight, based on total weight of the monomers. Amounts less than 5 percent result in brittle coatings, whereas amounts greater than 70 percent result in poor detergent resistance.

In addition to the vinyl aromatic compounds and the esters of acrylic and methacrylic acid, other ethylenically unsaturated copolymerizable monomers may be used. Examples include nitriles such as acrylonitrile, vinyl and vinylidene halides such as vinyl chloride and vinylidene fluoride and vinyl esters such as vinyl acetate. These additional monomers are present in amounts of about 0 to 40, preferably from 0 to 30 percent by weight based on total weight of monomers.

In preparing the acid group-containing acrylic polymer, the various monomers are mixed together and are reacted by conventional free radical initiated polymerization processes. Among the free radical initiators which may be used are benzoyl peroxide, tertiary-butyl hydroperoxide, ditertiarybutyl peroxide, azobis(2-methylpropionitrile), and so forth. The polymerization is preferably carried out in solution using a solvent in which the monomers are soluble such as toluene or xylene. At the completion of the polymerization, the reaction mixture can be devolatilized such as by placing under vacuum to remove the organic solvent and recovering the polymer as a solid material. Alternately, the polymer can be precipitated and subsequently dried. Usually, the devolatilized polymer will contain less than 1 percent by weight of materials that volatilize at the temperatures used for curing the coatings.

The acid group-containing acrylic polymer can also be prepared by emulsion polymerization, suspension polymerization, bulk polymerization or suitable combinations thereof. These techniques are well known in the art.

The acid group-containing acrylic polymer is preferably used in amounts of about 40 to 80, more preferably 50 to 70 percent by weight based on weight of resin solids. Amounts less than 40 percent by weight are not preferred because of poor heat and color stability, whereas amounts greater than 80 percent by weight result in poor flexibility and corrosion resistance.

Besides the carboxylic acid group-containing copolymer, the thermosetting powder coating composition of the invention preferably contains another acid group-containing material which is either a dibasic acid derived from a C_4 to C_{20} aliphatic dicarboxylic acid or a carboxylic acid group-terminated polyester. These particular materials are desirable because they provide flexibility and impact resistance in the resultant coating. Among the aliphatic dicarboxylic acids which may be used include adipic acid, subaric acid, azelaic acid, sebacic acid, and dodecanedioic acid. Preferably, the aliphatic dicarboxylic acid is a solid at room temperature.

Among the carboxylic acid group-containing polyesters which may be used are those based on condensing aliphatic dihydric alcohols with aliphatic and/or aromatic dicarboxylic acids. Examples of suitable aliphatic dihydric alcohols include ethylene glycol, propylene glycol, butylene glycol, 1,6-hexylene glycol, neopentyl glycol and the like. Suitable polycarboxylic acids include succinic acid, adipic acid, azelaic acid, sebacic acid, phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid and the like. These materials are preferably solid materials at room temperature and are commercially available from manufacturers such as Ciba Geigy Corporation under the trademark ARAKOTE resins, particularly ARAKOTE 3001.

The amount of aliphatic dicarboxylic acid or carboxylic acid group-terminated polyester ranges from 0 to 30, preferably 1 to 25 percent by weight based on weight of resin solids. Amounts greater than 30 percent by weight result in poor chemical resistance.

Besides the acid group-containing materials, the thermosetting powder coating compositions also contain an epoxy component which is a blend of two epoxy resins, an epoxy novolac resin which is compatible with the acid group-containing acrylic polymer and an epoxy resin which is incompatible with the acid group-containing acrylic polymer. Compatibility is determined by blending about 70 percent by weight of the acid group-containing acrylic polymer with 30 percent by weight of the particular epoxy and drawing down on a glass panel. The incompatible epoxy resins will be evidenced by a translucence or opaqueness in the coating, whereas the compatible epoxy resin will give a clear coating.